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Stereoselective synthesis of oxazolidines from 2-amino-2-deoxy-D-allose derivatives and their reactivity with nucleophiles†

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Abstract—The use of 2-amino-2-deoxy-D-allose in the synthesis of oxazolidines is described. The reaction takes place with total stereoselectivity in the preparation of both simple oxazolidines (from aldehydes as reagent) and bicyclic oxazolidines (from chlorocarbonyl compounds and keto-acids as reagents). The reactivity of the obtained oxazolidines with hydride and alkylmagnesium chlorides is also described. © 2001 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

The highly stereoselective condensation of carbonyl compounds (mainly aldehydes) with chiral β-aminoalcohols is of considerable interest as the 1,3-oxazolidines obtained are important chiral intermediates used in numerous asymmetric transformations. Neelakatan[2] described the synthesis and stereochemistry of these heterocycles (obtained by reaction between ephedrine and aromatic aldehydes) in 1971. Since then, numerous research groups have concentrated on broadening their use as chiral adjutants.

Diastereoselective addition of nucleophilic agents to the amino-bearing carbon gives an attractive approach to the asymmetric synthesis of chiral amines with good stereochemical control. Numerous works have been published on this topic, aimed partly at obtaining new chiral nitrogenated compounds (optically active amines,[3,4] α-aminoaldehydes,[5] etc.) and partly at a deeper understanding of the addition mechanism and the factors affecting the degree of stereoselection obtained (groups present in the heterocycle, nature of nucleophile used, solvent, temperature, etc.).[6–8] At the same time, various asymmetric transformations (Diels–Alder cycloadditions,[9] nucleophile addition,[10,11] epoxidations,[12] etc.) have been carried out on α,β-unsaturated carbonyl compounds derived from chiral oxazolidines obtained via condensation with chiral β-aminoalcohols.

Meyers et al.[13] described the asymmetric synthesis of bicyclic compounds having an oxazolidine ring fused to one of lactam, by condensation of the keto-acid with chiral β-aminoalcohols, generating in the process a new chiral centre with high stereoselectivity, the final diastereoisomeric excess depending on the nature of the precursor aminoalcohol substituents and their configuration, and on the cyclisation procedure used.[14–17]

The addition of hydrides to lactams with different substituents in the angular position gives different compounds depending on the nature of the hydride. Thus, the addition of lithium aluminium hydride yields the totally reduced compound, and in all cases, the configuration[18] of the lactam stereocentre is retained.

As part of our work, we have used 2-aminosugars with *gluco*, *allo* and *altro* configurations as chiral starting materials in the synthesis of different compounds (2-aminoglycals,[19] 2-nitrosugars,[20] and compounds with potential anti-cancer activity[21–23]). In previous papers we have described the synthesis of oxazolidines from 2-amino-2-deoxy-D-glucose derivatives with different groups on C-(2) of the oxazolidine ring,[1,24,25] and the reactivity of these compounds with nucleophiles.[26]

Herein, we describe the stereoselective synthesis of oxazolidines and bicyclic oxazolidines from 2-amino-2-deoxy-D-allose derivatives **1**–**6**, and their reactivity with hydrides and alkylmagnesium chlorides.

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† Oxazolidines from sugars, part 5. For part 4, see Ref. 1

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2. Results and discussion

The alkyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-β-D-allopyranosides **7** and **8** were obtained in good yield from the benzyl or dodecyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranosides **1**[27] and **2**[28] by reaction with dibromomethane under phase-transfer conditions, using a methodology previously described by our research group for obtaining oxazolidines derived from 2-amino-2-deoxy-D-glucose[25,26] (Scheme 1). The NMR spectra showed the signals corresponding to the methylidene group, introduced in the reaction. In the ^{1}H spectra, a singlet at 5.13 ppm for compound **7** and a double doublet (AB system) at 5.16 ppm for compound **8** were observed. The ^{13}C spectra showed signals at 80.5 and 79.8 ppm for compounds **7** and **8**, respectively.

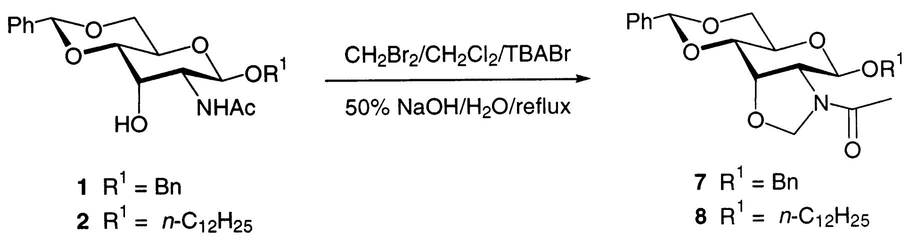
The preparation of *N*-alkyloxazolidines and *N*-acyloxazolidines, either mono- or disubstituted on C-(2) of the oxazolidine ring, was carried out by reaction of the alkyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-β-D-allopyranosides **3** and **4** or the alkyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranosides **5**[27] and **6**[21] with an aldehyde or ketone in the absence of an alkali.

The synthesis of compound **10** was carried out from **5** in two steps (Scheme 2). The treatment of **5** with acetone–dichloromethane (1:1) containing magnesium sulphate as a dehydrating agent gave oxazolidine **9**, characterised by its mass spectrum {MS (CI) *m*/*z* 398 (100%) $[M+H]^+$}. It was used without further purification because of its low stability (oxazolidine $\rightleftharpoons$ imine equilibrium has been described for compounds with this structure).[2] The reaction of **9** with acetyl chloride/pyridine in dichloromethane yielded compound **10** (65% from **5**). The NMR data confirm the presence of isopropylidene and acetyl groups, three singlets at 2.18, 1.58 and 1.47 ppm in the ^{1}H spectrum, and 168.4, 96.9, 26.7, 24.3 and 23.8 ppm in the ^{13}C spectrum.

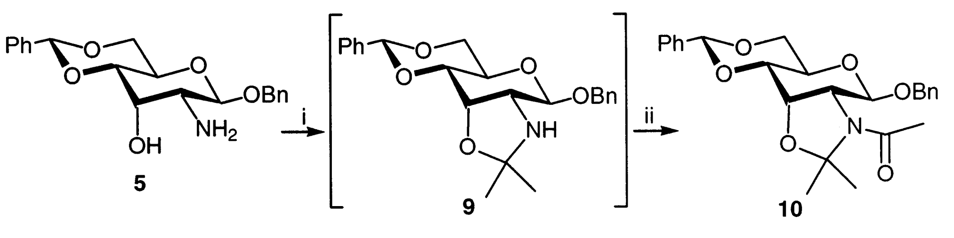
We also synthesised another set of oxazolidines which were obtained from the condensation of 2-ethylamino derivatives **3** and **4** with aldehydes. The products, **11**–**16**, present a stereogenic centre on C-(2) of the oxazolidine ring formed (Scheme 3). The reaction was carried out with **3** or **4** and the aldehyde in dichloromethane containing 4 Å molecular sieves. Compounds **11**–**16** were formed with complete stereoselectivity in these reactions (the NMR spectra of the bulk reaction indicated the presence of a single stereoisomer in each case). NOE and NOESY experiments allowed us to assign the (*S*)-configuration for the stereogenic centre formed in these reactions. Compounds **3** and **4** were obtained from the corresponding *N*-acetyl derivatives **1** and **2** by reduction with lithium aluminium hydride under standard conditions.

We have also obtained the bicyclic oxazolidines **17**–**29** from compounds **5** and **6**. In **17**–**29** the second cycle, fused to the oxazolidine ring, was formed in the reaction. These compounds had a trialkylamine structure (bicyclic pyrrolidines **17**–**21**) when a γ-chlorocarbonyl compound was used, or an *N*,*N*-dialkylamide structure (bicyclic lactams **22**–**29**), when a γ- or δ-keto-acid was used in the condensation reaction.

The bicyclic pyrrolidines **17**–**21** were prepared by condensation of compounds **5** or **6** and the corresponding γ-chlorocarbonyl compound at room temperature in dichloromethane in the presence of triethylamine (Scheme 4), as described by Pedrosa et al.[29] for the reaction of (*R*)-phenylglycinol with dialkyl γ- and δ-chloroketones. The γ-chlorocarbonyl compounds used in this study were an aldehyde, a methylketone, and a phenylketone. The reaction times were longest when we used 4-chlorobutyrophenone. The NMR spectra of the bulk reaction indicated the presence of a single stereoisomer in each case, and the condensation took place with total diastereoselectivity. NOESY experiments showed that the group on the angular carbon always had the same spatial orientation (*cis* with respect to H-1 of the sugar), independently of its nature ($R^2 = H$, Me, Ph).



Scheme 1.



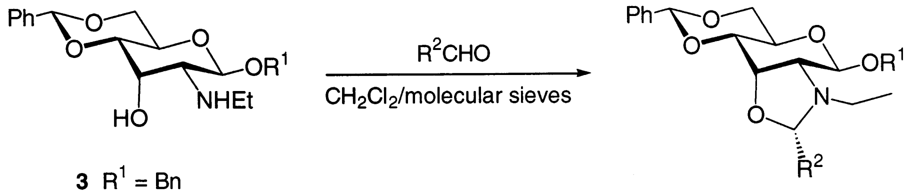
Scheme 2. (i) Acetone/CH_2Cl_2/$MgSO_4$. (ii) AcCl/Py/CH_2Cl_2.

The reaction of compounds **5** and **6** with γ- and δ-keto-acids gave the bicyclic lactams **22**–**29** with total stereoselectivity (NMR analysis of the crude reaction mixture) and a configuration for the new stereogenic centre with *cis* relationship between H-1 of the sugar and the substituent on the bridgehead carbon (R^2 group) in all compounds obtained (NOE and NOESY experiments) (Scheme 5). When the reaction was carried out in dichloromethane containing 4 Å molecular sieves[30] (method A), only the bicyclic lactams **22**, **24**, and **26** were obtained using 3-acetylpropionic acid or 4-acetylbutyric acid as reagents. The use of 3-benzoylpropionic acid, 4-benzoylbutyric acid, 2-carboxybenzaldehyde or 2-acetylbenzoic acid led to undesired compounds. In some cases we detected the formation of a non-cyclic amide, probably due to the lower reactivity of the carbonyl group linked to an aromatic ring.

We used another procedure[13,14] (method B) in the preparation of bicyclic lactams. A solution of compound **5** or **6**, the appropriate γ- or δ-keto-acid and *p*-toluenesulphonic acid in toluene was heated under reflux in a Dean–Stark apparatus to afford compounds **23**, **25** and **27**–**29** after 12 h.

We have also studied the reaction of some oxazolidines and bicyclic oxazolidines with lithium aluminium hydride and alkylmagnesium chlorides, varying the reaction conditions (Table 1). The reaction of compounds **7**, **10** and **11** with $LiAlH_4$ in THF gave, respectively, compounds **30**, **32** and **33** by reductive opening of the oxazolidine ring (Scheme 6). Compound **7** was reduced more quickly than **10** and **11**. The preparation of **32** from **10** and $LiAlH_4$/THF was carried out via **31**, characterised by its mass spectrum {MS (CI) *m*/*z* 498 $[M+H]^+$ (10%)} and its ^1H NMR (two singlets at 1.56 and 1.44 ppm corresponding to the isopropylidene group, and two multiplets at 2.56 and 1.09 ppm corresponding to the ethyl group). Stirring **31** for 48 h with $LiAlH_4$ gave the ring opened **32**. The ^1H NMR confirmed the presence of the isopropyl group, with a multiplet at 3.16 ppm and a doublet at 0.96 ppm. Reaction of **13** in toluene with *tert*-BuMgCl/THF over two days led to compounds **34** (Scheme 6) as a stereoisomeric mixture with a 76% diastereomeric excess.

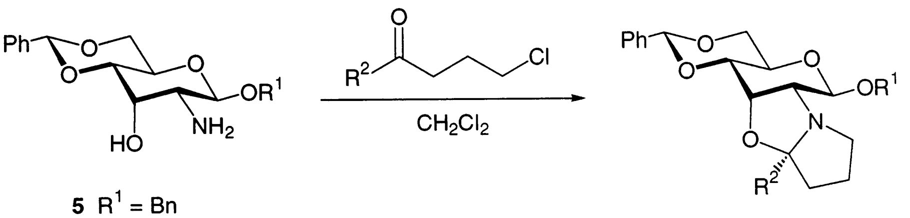
The reaction of $LiAlH_4$ and MeMgCl with the bicyclic oxazolidines **17**, **18** and **22** gave the compounds **35** and **36** (Scheme 7). Table 1 firstly shows that the reactions carried out with simple oxazolidines are slower than those with bicyclic oxazolidines having a bridgehead substituent, R^2. Secondly, it is notable that compounds **35** and **36** are epimers at C-(2) of the pyrrolidine ring and, given that they are obtained from compounds **17** and **18** (or **22**) stereochemically pure with the configuration of the angular carbon of the bicyclic system perfectly defined, it is deduced that the reactions with $LiAlH_4$ and MeMgCl follow the same stereochemical course. Various authors[18,29,31] have demonstrated that the reductive ring opening of the *N*,*O*-acetal moiety in bicyclic pyrrolidines and bicyclic lactams takes place with retention of the configuration of the bridgehead



3 R^1 = Bn
4 R^1 = *n*-$C_{12}H_{25}$

11 R^1 = Bn , R^2 = Me
12 R^1 = Bn , R^2 = Et
13 R^1 = Bn , R^2 = *i*-Pr
14 R^1 = Bn , R^2 = *trans*-PhCH=CH
15 R^1 = *n*-$C_{12}H_{25}$, R^2 = Et
16 R^1 = *n*-$C_{12}H_{25}$, R^2 = Bn

Scheme 3.



5 R^1 = Bn
6 R^1 = *n*-$C_{12}H_{25}$

17 R^1 = Bn , R^2 = H
18 R^1 = Bn , R^2 = Me
19 R^1 = Bn , R^2 = Ph
20 R^1 = *n*-$C_{12}H_{25}$, R^2 = Me
21 R^1 = *n*-$C_{12}H_{25}$, R^2 = Ph

Scheme 4.

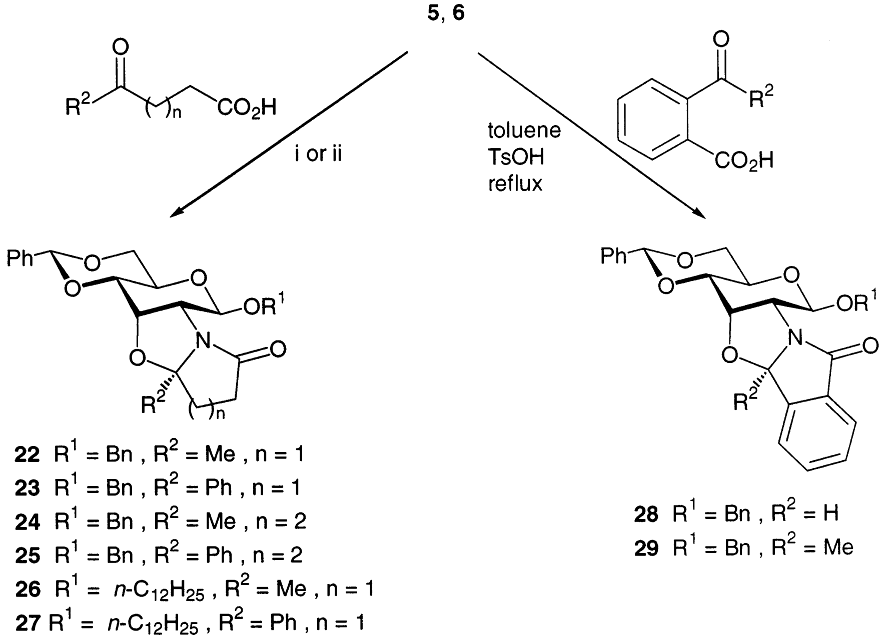
carbon of the bicyclic system. Consequently, we could easily assign the absolute configurations of compounds **35** and **36**. However, the $LiAlH_4$ reduction of bicyclic oxazolidines substituted with an aromatic ring at the angular position (**19**, **21**, **23**, **25**, **27**, **28** and **29**) led to inseparable mixtures of products.

In conclusion, we present a stereoselective procedure for the synthesis of oxazolidines derived from alkyl allopyranosides, with good yields, in which the 2-amino-2-deoxy-D-allose moiety acts as a good chiral adjutant, both in the formation of simple oxazolidines and in that of bicyclic pyrrolidines and bicyclic lactams. The reactivity of the oxazolidines with lithium aluminium hydride and Grignard reagents depends heavily on the C-(2) substituent of the oxazolidine ring. When C-(2) was unsubstituted or substituted with an alkyl group, the reaction took place with good stereoisomeric control, whereas when the C-(2) substituent of the oxazolidine ring was an aryl group, the reaction led to a mixture of products.

3. Experimental

3.1. General

Evaporations were conducted under reduced pressure. Preparative chromatography was performed on Silica Gel 60 (E. Merck). Kieselgel 60 F_{254} (E. Merck) was used for TLC. Melting points are uncorrected. Optical rotations were obtained on a Bellingham+Stanley Ltd P-20 polarimeter at 25°C. Infrared (IR) spectra were obtained on a Jasco FT/IR-410 spectrophotometer. Mass spectra were recorded on a Micromass AUTOSPECQ mass spectrometer, CI at 150 eV, and HR mass measurements with resolutions of 10,000. NMR spectra were recorded at 25°C on a Bruker



22 R^1 = Bn , R^2 = Me , n = 1
23 R^1 = Bn , R^2 = Ph , n = 1
24 R^1 = Bn , R^2 = Me , n = 2
25 R^1 = Bn , R^2 = Ph , n = 2
26 R^1 = n-$C_{12}H_{25}$, R^2 = Me , n = 1
27 R^1 = n-$C_{12}H_{25}$, R^2 = Ph , n = 1

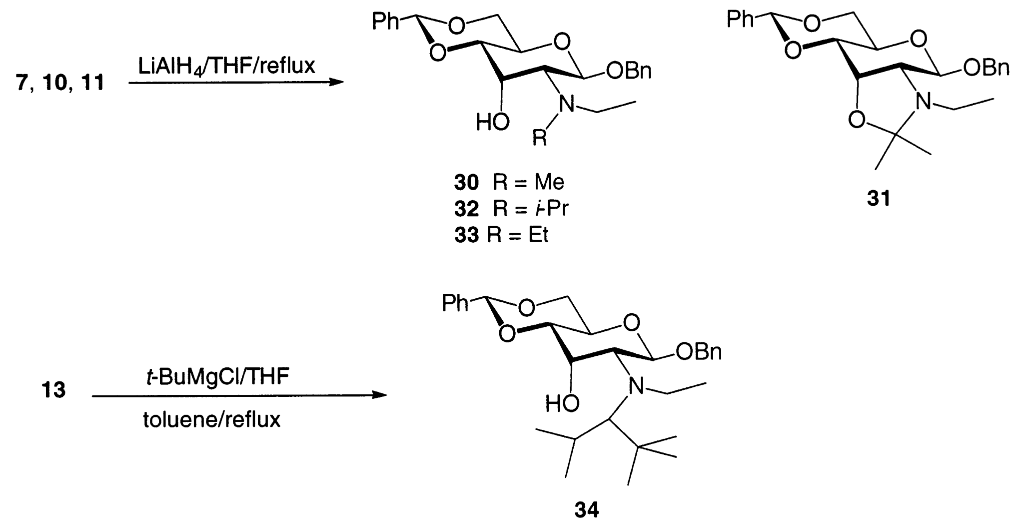
28 R^1 = Bn , R^2 = H
29 R^1 = Bn , R^2 = Me

Scheme 5. (i) Method A: CH_2Cl_2/molecular sieves/2 weeks (**22**, **24**, **26**). (ii) Method B: toluene/TsOH/reflux/12 hours (**23**, **25** **27**–**29**).

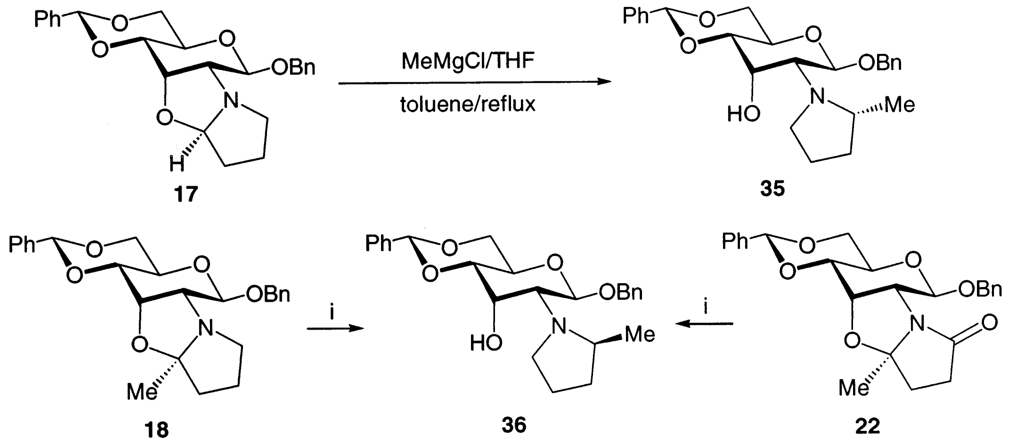
Table 1. Reaction of oxazolidines with $LiAlH_4$ and RMgX

Entry	Oxazolidine	Reagent	Molar relationship oxazolidine/reagent	Time reaction (h)	Reaction product	Yield[a] (%)	d.e.[b] (%)
1	**7**	$LiAlH_4$	1:5	15	**30**	70	—
2	**10**	$LiAlH_4$	1:5	15	**31**[c]	72	—
3	**10**	$LiAlH_4$	1:5	48	**32**	56	—
4	**11**	$LiAlH_4$	1:10	48	**33**	53	—
5	**13**	t-BuMgCl	1:4	48	**34**	68	76
6	**17**	MeMgCl	1:5	4	**35**	71	72
7	**17**	MeMgCl	1:5	72[d]	**35**	76	84
8	**18**	$LiAlH_4$	1:2	15	**36**	94	100
9	**22**	$LiAlH_4$	1:10	5	**36**	78	80

[a] Yields refer to compounds obtained in each reaction after isolation and purification.
[b] Determined by integration in ^1H NMR spectra of reaction mixtures.
[c] Detected by MS and characterised by ^1H NMR.
[d] Reaction at room temperature.



Scheme 6.



Scheme 7. (i) $LiAlH_4$/THF/reflux.

AC-200 spectrometer at 200 MHz for ^{1}H and 50 MHz for ^{13}C, and on a Bruker AMX-500 spectrometer at 500 MHz for ^{1}H and 125 MHz for ^{13}C. The chemical shifts are reported in ppm on the δ scale relative to TMS.

3.2. Alkyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-β-D-allopyranosides 3 and 4

A solution of alkyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **1** or **2** (10.0 mmol) in dry THF (200 mL) was stirred under an argon atmosphere at reflux, 1 M solution of lithium aluminium hydride in THF (15.0 mmol) was added, and the reaction mixture stirred under reflux overnight and then left to cool to room temperature. Saturated aqueous sodium sulphate solution (4.5 mL) was added dropwise. The solid was removed by filtration and washed with anhydrous THF. The filtrate was concentrated to dryness to give a solid which was recrystallised from 96% ethanol.

3.2.1. Benzyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-β-D-allopyranoside 3. Yield 3.35 g (87%); mp 148–149°C; $[\alpha]_D$ −89.8 (*c* 0.5, CH_2Cl_2); MS (CI) *m*/*z* 386 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.56 (PhC$\underline{H}$), 4.91 (d, 1H, J_{gem} 11.6 Hz, OC$\underline{H}_A$H$_B$Ph), 4.69 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.56 (d, 1H, J_{gem} 11.6 Hz, OCH$_A\underline{H}_B$Ph), 4.40 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.2 Hz, H-6$_e$), 4.24 (t, 1H, $J_{2,3}=J_{3,4}$ 2.6 Hz, H-3), 4.07 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.7 Hz, $J_{5,6e}$ 5.0 Hz, H-5), 3.78 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.2 Hz, H-6$_a$), 3.62 (dd, 1H, $J_{3,4}$ 2.6 Hz, $J_{4,5}$ 9.4 Hz, H-4), 2.7–2.5 (m, 3H, H-2, NC$\underline{H}_2$CH$_3$), 1.08 (t, 3H, J 7.1 Hz, NCH$_2$C$\underline{H}_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.2–126.3 (2Ph), 102.2 (Ph$\underline{C}$H), 99.9 (C-1), 79.5 (C-4), 71.4 (O$\underline{C}$H$_2$Ph), 69.1 (C-6), 65.1 (C-3), 63.2 (C-5), 61.6 (C-2), 40.5 (N$\underline{C}$H$_2$CH$_3$), 15.3 (NCH$_2\underline{C}$H$_3$). HRMS (CI): $[M+H]^+$, found 386.196060. $C_{22}H_{28}NO_5$ requires 386.196748. Anal. calcd for $C_{22}H_{27}NO_5$: C, 68.55; H, 7.06; N, 3.63. Found: C, 68.27; H, 7.01; N, 3.63.

3.2.2. 1-Dodecyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-β-D-allopyranoside 4. Yield 3.80 g (82%); mp 122–123°C; $[\alpha]_D$ −60.6 (*c* 0.5, CH_2Cl_2); MS (CI) *m*/*z* 464 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.53 (PhC$\underline{H}$), 4.58 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.35 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.1 Hz, H-6$_e$), 4.23 (t, 1H, $J_{2,3}=J_{3,4}$ 2.6 Hz, H-3), 4.03 (dt, 1H, $J_{5,6e}$ 5.0 Hz, $J_{4,5}=J_{5,6a}$ 9.7 Hz, H-5), 3.86 (m, 1H, OC$\underline{H}_A$H$_B$R), 3.74 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.2 Hz, H-6$_a$), 3.57 (dd, 1H, $J_{3,4}$ 2.5 Hz, $J_{4,5}$ 9.4 Hz, H-4), 3.45 (m, 1H, OCH$_A\underline{H}_B$R), 2.7–2.5 (m, 3H, H-2, NC$\underline{H}_2$CH$_3$), 1.6–1.2 [m, 20H, (CH$_2$)$_{10}$], 1.11 (t, 3H, J 7.1 Hz, NCH$_2$C$\underline{H}_3$), 0.86 (t, 3H, *J* 6.5 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.2–126.2 (Ph), 102.1 ($\underline{C}HPh$), 100.7 (C-1), 79.6 (C-4), 70.2 ($O\underline{C}H_2R$), 69.1 (C-6), 65.1 (C-3), 63.1 (C-5), 61.7 (C-2), 40.6 ($N\underline{C}H_2CH_3$), 31.8–22.6 [$(CH_2)_{10}$], 15.3 ($NCH_2\underline{C}H_3$), 14.1 (CH_3). HRMS (CI): [M+H]$^+$, found 464.338053. $C_{27}H_{46}NO_5$ requires 464.337599. Anal. calcd for $C_{27}H_{45}NO_5$: C, 69.94; H, 9.78; N, 3.02. Found: C, 69.62; H, 9.83; N, 3.00.

3.3. Formation of *N*-acetyloxazolidines from alkyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside and dibromomethane

3.3.1. Alkyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-β-D-allopyranosides 7 and 8. To a solution of the alkyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **1** or **2** (2.5 mmol) in distilled dichloromethane (50 mL), dibromomethane (50 mL), 50% aqueous sodium hydroxide solution (100 mL) and tetrabutylammonium bromide (6.5 mg, 0.02 mmol) were added. The reaction mixture was stirred vigorously under reflux for 2 days, then cooled to room temperature. The organic phase was washed with water until neutral, dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on silica gel.

3.3.2. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-β-D-allopyranoside 7. Column chromatography using hexane–ethyl acetate (15:10) as eluent yielded 0.85 g (83%); mp 86–87°C; $[\alpha]_D$ −68.0 (*c* 0.5, CH_2Cl_2); MS (CI) *m*/*z* 412 (41%) [M+H]$^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, Ph), 5.57 ($PhC\underline{H}$), 5.13 (s, 2H, OCH_2N), 4.92 (d, 1H, J_{gem} 11.3 Hz, $OC\underline{H}_AH_BPh$), 4.64 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.57 (d, 1H, J_{gem} 11.3 Hz, $OCH_A\underline{H}_BPh$), 4.5–4.4 (m, 2H, H-3, H-6$_e$), 4.0–3.7 (m, 4H, H-2, H-4, H-5, H-6$_a$), 2.14 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.3 (C=O), 136.7–126.3 (2Ph), 102.8 ($Ph\underline{C}H$), 100.7 (C-1), 80.5 (OCH_2N), 76.6 (C-4), 76.4 (C-3), 71.9 ($O\underline{C}H_2Ph$), 69.0 (C-6), 63.6 (C-5), 60.0 (C-2), 22.6 (CH_3). Anal. calcd for $C_{23}H_{25}NO_6$: C, 67.14; H, 6.12; N, 3.40. Found: C, 66.91; H, 6.21; N, 3.41.

3.3.3. 1-Dodecyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-methylidene-β-D-allopyranoside 8. Column chromatography using hexane–ethyl acetate (2:1) as eluent yielded 0.90 g (74%) as a syrup; MS (CI) *m*/*z* 490 (45%) [M+H]$^+$; ^1H NMR (250 MHz, $CDCl_3$): δ 7.5–7.3 (m, 5H, Ph), 5.55 (s, 1H, $PhC\underline{H}$), 5.16 (dd, 2H, J_{gem} 10.8 Hz, OCH_2N), 4.51 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.4–4.3 (m, 2H, H-3, H-6$_e$), 4.0–3.7 (m, 5H, H-2, H-4, H-5, H-6$_a$, $OC\underline{H}_AH_BR$), 3.47 (m, 1H, $OCH_A\underline{H}_BR$), 2.19 (s, 3H, CH_3CON), 1.6–1.2 [m, 20H, $(CH_2)_{10}$], 0.86 (m, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.6 (C=O), 136.4–125.7 (Ph), 101.8 ($Ph\underline{C}H$), 101.2 (C-1), 79.8 (OCH_2N), 76.0 (C-4), 75.7 (C-3), 69.9 (OCH_2R), 68.4 (C-6), 62.8 (C-5), 59.3 (C-2), 31.3–22.1 [$(CH_2)_{10}$], 21.9 ($\underline{C}H_3CON$), 13.6 (CH_3). HRMS (CI): [M+H]$^+$, found 490.316780. $C_{28}H_{44}NO_6$ requires 490.316864.

3.4. Formation of *N*-acetyloxazolidine from benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside, acetone and acyl chlorides

3.4.1. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-isopropylidene-β-D-allopyranoside 10. A solution of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **5** (1.0 g, 2.8 mmol) in dry acetone (100 mL) was stirred at room temperature for 3 h. Distilled dichloromethane (100 mL) and anhydrous magnesium sulphate (2.0 g) were added, and the suspension was stirred for two weeks. Then, the reaction mixture was filtered through a pad (4 cm diameter×0.5 cm height) of kieselguhr and the solvent was evaporated to dryness. The compound obtained, benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-isopropylidene-β-D-allopyranoside **9** {MS (CI) *m*/*z* 398 (100%) [M+1]$^+$}, was used without further purification. To a solution of **9** in distilled dichloromethane (100 mL) at 0°C, dry pyridine (10 mL) and acetyl chloride (5.0 mmol) were added. The reaction mixture was stirred overnight at room temperature, and then poured into ice water. The organic phase was washed successively with water, saturated aqueous sodium bicarbonate solution, and washed with further water. The solution was dried ($MgSO_4$), filtered, and evaporated to dryness. The solid obtained was purified by column chromatography using hexane–ethyl acetate (16:10) as the eluent, yielding 0.80 g (65%); mp 149–150°C; $[\alpha]_D$ −53.9 (*c* 0.5, CH_2Cl_2); MS (CI) *m*/*z* 440 (100%) [M+H]$^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.56 (s 1H, $PhC\underline{H}$), 4.89 (d, 1H, J_{gem} 11.7 Hz, $OC\underline{H}_AH_BPh$), 4.65 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.59 (d 1H, J_{gem} 11.7 Hz, $OCH_A\underline{H}_BPh$), 4.5–4.4 (m, 2H, H-3, H-6$_e$), 4.0–3.7 (m, 4H, H-5, H-2, H-4, H-6$_a$), 2.18 (s, 3H, CH_3CO), 1.58, 1.47 [2s, 6H, $OC(CH_3)_2N$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.4 (C=O), 136.8–126.4 (2Ph), 102.8 ($Ph\underline{C}H$), 100.6 (C-1), 96.9 [$O\underline{C}(CH_3)_2N$], 76.8 (C-4), 72.4 (C-3), 71.3 ($O\underline{C}H_2Ph$), 69.1 (C-6), 63.5 (C-5), 61.8 (C-2), 26.7, 23.8 [$OC(\underline{C}H_3)_2N$], 24.3 ($CO\underline{C}H_3$). Anal. calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.17; H, 6.66; N, 3.28.

3.5. Formation of oxazolidine rings from alkyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-β-D-allopyranosides and aldehydes

To a solution of the alkyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-β-D-allopyranoside **3** or **4** (1.0 mmol) in distilled dichloromethane (50 mL), containing 4 Å molecular sieves, the corresponding aldehyde (2.5 mmol) was added. The suspension was stirred until completion of the reaction (1–2 weeks, TLC). The solid was removed by filtration, washed with dichloromethane, and the organic phase was evaporated to dryness.

3.5.1. (*S*)-Benzyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-2-*N*-3-*O*-ethylidene-β-D-allopyranoside 11. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl ether (4:1) as eluent, yielding 0.25 g (61%); mp 85–86°C; $[\alpha]_D$ −104.6 (*c* 0.7, CH_2Cl_2); MS (CI) *m*/*z* 412 [M+H]$^+$

(100%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.6–7.3 (m, 10H, 2Ph), 5.57 (s, 1H, PhC$\underline{H}$), 4.90 (d, 1H, J_{gem} 12.2 Hz, OC$\underline{H}_A$H$_B$Ph), 4.66 (d, 1H, J_{gem} 12.2 Hz, OCH$_A\underline{H}_B$Ph), 4.59 (d, 1H, $J_{1,2}$ 6.0 Hz, H-1), 4.4–4.3 (m, 2H, H-6$_e$, OC$\underline{H}$(CH$_3$)N), 4.28 (dd, 1H, $J_{2,3}$ 5.5 Hz, $J_{3,4}$ 3.3 Hz, H-3), 4.00 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 5.1 Hz, H-5), 3.94 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{4,5}$ 9.7 Hz, H-4), 3.75 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.1 Hz, H-6$_a$), 3.04 (t, 1H, $J_{1,2}=J_{2,3}$ 5.8 Hz, H-2), 2.66 (q, 2H, J 7.2 Hz, NC$\underline{H}_2$CH$_3$), 1.33 [d, 3H, J 5.3 Hz, OCH(C$\underline{H}_3$)N], 1.11 (t, 3H, J 7.2 Hz, NCH$_2$C$\underline{H}_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 137.4–126.3 (2Ph), 102.5 (Ph$\underline{C}$H), 102.4 (C-1), 95.1 [O$\underline{C}$H(CH$_3$)N], 76.8 (C-4), 73.5 (C-3), 70.7 (O$\underline{C}$H$_2$Ph), 69.5 (C-6), 66.2 (C-2), 62.7 (C-5), 47.3 (N$\underline{C}$H$_2$CH$_3$), 21.6 [OCH($\underline{C}$H$_3$)N], 14.2 (NCH$_2\underline{C}$H$_3$). Anal. calcd for C$_{24}$H$_{29}$NO$_5$: C, 70.05; H, 7.10; N, 3.40. Found: C, 70.35; H, 7.25; N, 3.37.

3.5.2. (*S*)-Benzyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-2-*N*-3-*O*-propylidene-β-D-allopyranoside 12. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl ether (45:10) as eluent, yielding 0.30 g (71%); mp 112–113°C; $[\alpha]_D$ −98.1 (*c* 1.0, CH$_2$Cl$_2$); MS (CI) *m*/*z* 426 (100%) [M+H]$^+$. ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.54 (s, 1H, PhC$\underline{H}$), 4.87 (d, 1H, J_{gem} 12.3 Hz, OC$\underline{H}_A$H$_B$Ph), 4.64 (d, 1H, J_{gem} 12.3 Hz, OCH$_A\underline{H}_B$Ph), 4.54 (d, 1H, $J_{1,2}$ 6.7 Hz, H-1), 4.38 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.7 Hz, H-6$_e$), 4.3–4.2 [m, 2H, H-3, OC$\underline{H}$(CH$_2$CH$_3$)N], 3.9–3.8 (m, 2H, H-4, H-5), 3.72 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.7 Hz, H-6$_a$), 2.98 (dd, 1H, $J_{1,2}$ 6.7 Hz, $J_{2,3}$ 5.3 Hz, H-2), 2.60 (m, 2H, NC$\underline{H}_2$CH$_3$), 1.57 [m, 2H, OCH(C$\underline{H}_2$CH$_3$)N], 1.09 (t, 3H, J 7.2 Hz, NCH$_2$C$\underline{H}_3$), 0.90 [t, 3H, J 7.5 Hz, OCH(CH$_2$C$\underline{H}_3$)N]. ^{13}C NMR (50 MHz, CDCl$_3$): δ 137.5–126.4 (2Ph), 102.6 (Ph$\underline{C}$H), 102.4 (C-1), 99.7 [O$\underline{C}$H(CH$_2$CH$_3$)N], 77.3 (C-4), 73.5 (C-3), 70.8 (O$\underline{C}$H$_2$Ph), 69.5 (C-6), 66.2 (C-2), 62.9 (C-5), 48.2 (N$\underline{C}$H$_2$CH$_3$), 28.6 [OCH($\underline{C}$H$_2$CH$_3$)N], 14.5 (NCH$_2\underline{C}$H$_3$), 8.9 [OCH(CH$_2\underline{C}$H$_3$)N]. Anal. calcd for C$_{25}$H$_{31}$NO$_5$: C, 70.56; H, 7.34; N, 3.29. Found: C, 70.36; H, 7.29; N, 3.38.

3.5.3. (*S*)-Benzyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-2-*N*-3-*O*-isobutylidene-β-D-allopyranoside 13. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl ether (7:1) as eluent, yielding 0.25 g (57%) as a syrup; MS (CI): *m*/*z* 440 (100%) [M+H]$^+$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.60 (s, 1H, PhC$\underline{H}$), 4.88 (d, 1H, J_{gem} 12.4 Hz, OC$\underline{H}_A$H$_B$Ph), 4.66 (d, 1H, J_{gem} 12.4 Hz, OCH$_A\underline{H}_B$Ph), 4.55 (s, 1H, $J_{1,2}$ 7.0 Hz, H-1), 4.39 (dd, 1H, $J_{5,6e}$ 5.0 Hz, $J_{6e,6a}$ 10.3 Hz, H-6$_e$), 4.22 (dd, 1H, $J_{2,3}$ 4.9 Hz, $J_{3,4}$ 3.3 Hz, H-3), 4.02 {d, 1H, J 5.7 Hz, OC$\underline{H}$[CH(CH$_3$)$_2$]N}, 3.90 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.8 Hz, $J_{5,6e}$ 5.0 Hz, H-5), 3.84 (dd,1H, $J_{3,4}$ 3.3 Hz, $J_{4,5}$ 9.6 Hz, H-4), 3.75 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.2 Hz, H-6$_a$), 2.97 (dd, 1H, $J_{1,2}$ 7.0 Hz, $J_{2,3}$ 5.0 Hz, H-2), 2.58 (m, 2H, NC$\underline{H}_2$CH$_3$), 1.64 {m, 1H, OCH[C$\underline{H}$(CH$_3$)$_2$]N}, 1.12 (t, 3H, J 7.1 Hz, NCH$_2$C$\underline{H}_3$), 0.93, 0.92 {2d, 6H, J 6.7 Hz, OCH[CH(C$\underline{H}_3$)$_2$]N}. ^{13}C NMR (50 MHz, CDCl$_3$): δ 137.3–126.2 (2Ph), 103.2 (Ph$\underline{C}$H), 102.1 (C-1), 101.9 {O$\underline{C}$H[CH(CH$_3$)$_2$]N}, 77.2 (C-4), 73.3 (C-3), 70.5 (O$\underline{C}$H$_2$Ph), 69.2 (C-6), 65.9 (C-2), 62.7 (C-5), 48.7 (N$\underline{C}$H$_2$CH$_3$), 33.5 {OCH[$\underline{C}$H(CH$_3$)$_2$]N}, 18.1, 17.4 {OCH[CH($\underline{C}$H$_3$)$_2$]N}, 14.4 (NCH$_2\underline{C}$H$_3$). HRMS (CI): [M+H]$^+$, found 440.242266. C$_{26}$H$_{34}$NO$_5$ requires 440.243699.

3.5.4. (*S*)-Benzyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-2-*N*-3-*O*-(*trans*-3-phenyl-2-propenylidene)-β-D-allopyranoside 14. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl ether (7:1) as eluent, yielding 0.25 g (50%); mp 120–121°C; $[\alpha]_D$ −140.0 (*c* 0.2, CHCl$_3$); MS (CI) *m*/*z* 500 (100%) [M+H]$^+$. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.5–7.3 (m, 15H, 3Ph), 6.65 (d, 1H, J_{trans} 15.8 Hz, CHCH=C$\underline{H}$Ph), 6.09 (dd, 1H, J_{trans} 15.8 Hz, J 6.6 Hz, CHC$\underline{H}$=CHPh), 5.56 (s, 1H, PhC$\underline{H}$), 4.90 (d, 1H, J_{gem} 12.2 Hz, OC$\underline{H}_A$H$_B$Ph), 4.76 (d, 1H, J 6.5 Hz, C$\underline{H}$CH=CHPh), 4.65 (d, 1H, J_{gem} 12.2 Hz, OCH$_A\underline{H}_B$Ph), 4.64 (d, 1H, $J_{1,2}$ 6.1 Hz, H-1), 4.4–4.3 (m, 2H, H-3, H-6$_e$), 4.0–3.9 (m, 2H, H-4, H-5), 3.73 (t, 1H, $J_{5,6e}=J_{6e,6a}$ 9.8 Hz, H-6$_a$), 3.15 (t, 1H, $J_{1,2}=J_{2,3}$ 5.9 Hz, H-2), 2.72 (q, 2H, J 7.2 Hz, NC$\underline{H}_2$CH$_3$), 1.09 (t, 3H, J 7.2 Hz, NCH$_2$C$\underline{H}_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 137.6–126.0 (3Ph), 133.4 (CHCH=$\underline{C}$HPh), 129.0 (CH$\underline{C}$H=CHPh), 102.6 (Ph$\underline{C}$H), 101.9 (C-1), 98.7 ($\underline{C}$HCH=CHPh), 77.0 (C-4), 73.7 (C-3), 70.8 (O$\underline{C}$H$_2$Ph), 69.6 (C-6), 66.0 (C-2), 62.8 (C-5), 47.2 (N$\underline{C}$H$_2$CH$_3$), 14.2 (NCH$_2\underline{C}$H$_3$). HRMS (EI): [M]$^{+\bullet}$, found 499.235940. C$_{31}$H$_{32}$NO$_5$ requires 499.235874.

3.5.5. (*S*)-1-Dodecyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-2-*N*-3-*O*-propylidene-β-D-allopyranoside 15. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl ether (8:1) as eluent, yielding 0.30 g (60%) as a syrup; MS (CI) *m*/*z* 504 (100%) [M+H]$^+$. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.5–7.3 (m, 5H, Ph), 5.53 (s, 1H, PhC$\underline{H}$), 4.42 (d, 1H, $J_{1,2}$ 6.8 Hz, H-1), 4.35 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.9 Hz, H-6$_e$), 4.3–4.2 [m, 2H, H-3, OC$\underline{H}$(CH$_2$CH$_3$)N], 4.0–3.8 (m, 3H, H-4, H-5, OC$\underline{H}_A$H$_B$R), 3.70 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 9.9 Hz, H-6$_a$), 3.46 (m, 1H, OCH$_A\underline{H}_B$R), 2.88 (dd, 1H, $J_{1,2}$ 6.8 Hz, $J_{2,3}$ 5.1 Hz, H-2), 2.57 (m, 2H, J 7.2 Hz, NC$\underline{H}_2$CH$_3$), 1.7–1.6 [m, 2H, OCH(C$\underline{H}_2$CH$_3$)N], 1.5–1.3 [m, 20H, (CH$_2$)$_{10}$], 1.10 (t, 3H, J 7.2 Hz, NCH$_2$C$\underline{H}_3$), 0.98 [t, 3H, J 7.4 Hz, OCH(CH$_2$C$\underline{H}_3$)N] 0.88 (m, 3H, CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 137.2–126.4 (Ph), 103.8 (Ph$\underline{C}$H), 102.6 (C-1), 99.6 [O$\underline{C}$H(CH$_2$CH$_3$)N], 77.3 (C-4), 73.7 (C-3), 70.3 (O$\underline{C}$H$_2$R), 69.5 (C-6), 66.2 (C-2), 62.7 (C-5), 48.0 (N$\underline{C}$H$_2$CH$_3$), 31.9–22.6 [(CH$_2$)$_{10}$], 28.6 [OCH($\underline{C}$H$_2$CH$_3$)N], 14.5 (NCH$_2\underline{C}$H$_3$), 14.1 (CH$_3$), 8.9 [OCH(CH$_2\underline{C}$H$_3$)N]. HRMS (CI): [M+H]$^+$, found 504.368496. C$_{30}$H$_{50}$NO$_5$ requires 504.368899.

3.5.6. (*S*)-1-Dodecyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-2-*N*-3-*O*-(2-phenylethylidene)-β-D-allopyranoside 16. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl ether (10:1) as eluent, yielding 0.40 g (71%) as a syrup; MS (CI) *m*/*z* 566 (100%) [M+H]$^+$. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.5–7.2 (m, 10H, 2Ph), 5.51 (s, 1H, PhC$\underline{H}$), 4.51 [t, 1H, J 4.2 Hz, OC$\underline{H}$(CH$_2$Ph)N], 4.30 (d, 1H, H-1), 4.17 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 10.0 Hz, H-6$_e$), 3.8–3.6 (m, 5H, H-3, H-5, H-4, H-6$_a$, OC$\underline{H}_A$H$_B$R), 3.20

(m, 1H, $\mathrm{OCH_A\underline{H}_BR}$), 2.98 [m, 2H, $\mathrm{OCH(C\underline{H}_2Ph)N}$], 2.79 (dd, 1H, $J_{1,2}$ 7.1 Hz, $J_{2,3}$ 5.0 Hz, H-2), 2.45 (m, 2H, $\mathrm{NC\underline{H}_2CH_3}$), 1.5–1.2 [m, 20H, $\mathrm{(CH_2)_{10}}$], 1.02 (t, 3H, J 7.1 Hz, $\mathrm{NCH_2C\underline{H}_3}$), 0.88 (m, 3H, $\mathrm{CH_3}$). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ 137.2–126.2 (2Ph), 103.8 ($\mathrm{Ph\underline{C}H}$), 102.5 (C-1), 98.6 [$\mathrm{O\underline{C}H(CH_2Ph)N}$], 77.3 (C-4), 73.8 (C-3), 70.4 ($\mathrm{OCH_2R}$), 69.4 (C-6), 66.1 (C-2), 62.8 (C-5), 47.9 ($\mathrm{N\underline{C}H_2CH_3}$), 41.3 [$\mathrm{OCH(C\underline{H}_2Ph)N}$], 31.9–22.6 [$\mathrm{(CH_2)_{10}}$], 14.5 ($\mathrm{NCH_2\underline{C}H_3}$), 14.1 ($\mathrm{CH_3}$). HRMS (EI): $[\mathrm{M}]^{+\bullet}$, found 565.375782. $\mathrm{C_{35}H_{51}NO_5}$ requires 565.376724.

3.6. General procedure for the formation of bicyclic pyrrolidines from alkyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranosides and γ-chlorocarbonyl compounds

To a solution of alkyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **5** or **6** (1.0 mmol) in distilled dichloromethane (15 mL), triethylamine (1.2 mmol) and the corresponding γ-chlorocarbonyl compound (1.2 mmol) were added. The solution was stirred at room temperature until completion of the reaction (1–2 weeks, TLC). Then, the solids were removed by filtration and the solution was washed successively with saturated aqueous solution of sodium bicarbonate and water, dried ($\mathrm{MgSO_4}$), filtered, and the filtrate evaporated to dryness. The solid obtained was purified by flash chromatography on silica gel.

3.6.1. (2*R*)-2,3-Propylen-(benzyl 2-amino-4,6-*O*-benzylidene-2,3-dideoxy-β-D-allopyranoside)[2,3-*d*][1,3]oxazolidine 17. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (27:10) as eluent, yielding 0.25 g (61%); mp 132–133°C; $[\alpha]_D$ −80.0 (*c* 0.6, $\mathrm{CHCl_3}$); MS (CI) *m*/*z* 410 (100%) $[\mathrm{M+H}]^+$. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.6–7.3 (m, 10H, 2Ph), 5.55 (s, 1H, $\mathrm{PhC\underline{H}}$), 5.20 (dd, 1H, OCHN), 4.92 (d, 1H, J_{gem} 11.8 Hz, $\mathrm{OC\underline{H}_AH_BPh}$), 4.68 (d, 1H, J_{gem} 11.8 Hz, $\mathrm{OCH_A\underline{H}_BPh}$), 4.55 (d, 1H, $J_{1,2}$ 6.9 Hz, H-1), 4.40 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 10.5 Hz, H-6$_e$), 4.30 (dd, 1H, $J_{2,3}$ 4.7 Hz, $J_{3,4}$ 2.6 Hz, H-3), 3.8–3.7 (m, 3H, H-4, H-5, H-6$_a$), 3.32 (dd, 1H, $J_{1,2}$ 6.9 Hz, $J_{2,3}$ 4.7 Hz, H-2), 3.25 (m, 1H, $\mathrm{C\underline{H}_AH_BN}$), 2.64 (m, 1H, $\mathrm{CH_A\underline{H}_BN}$), 2.2–1.7 [m, 4H, $\mathrm{(CH_2)_2}$]. ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): 137.4–126.4 (Ph), 102.6 ($\mathrm{Ph\underline{C}H}$), 100.6 (C-1), 99.3 (OCHN), 78.0 (C-4), 71.1 ($\mathrm{O\underline{C}H_2Ph}$), 70.9 (C-3), 69.3 (C-6), 69.1 (C-2), 62.8 (C-5), 53.7 ($\mathrm{CH_2N}$), 32,8, 24,1 [$\mathrm{(CH_2)_2}$]. HRMS (EI): $[\mathrm{M}]^+$, found 409.186911. $\mathrm{C_{24}H_{27}NO_5}$ requires 409.188923. Anal. calcd for $\mathrm{C_{24}H_{27}NO_5}$: C, 70.40; H, 6.65; N, 3.42. Found: C, 70.22; H, 6.68; N, 3.40.

3.6.2. (2*R*)-2-Methyl-2,3-propylen-(benzyl 2-amino-4,6-*O*-benzylidene-2,3-dideoxy-β-D-allopyranoside)[2,3-*d*][1,3] oxazolidine 18. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (2:1) as eluent, yielding 0.30 g (71%); mp 122–123°C; $[\alpha]_D$ −82.8 (*c* 0.4, $\mathrm{CH_2Cl_2}$); MS (CI) *m*/*z* 424 (100%) $[\mathrm{M+H}]^+$. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 7.5–7.3 (m, 10H, 2Ph), 5.54 (s, 1H, $\mathrm{PhC\underline{H}}$), 4.90 (d, 1H, J_{gem} 12.1 Hz, $\mathrm{OC\underline{H}_AH_BPh}$), 4.69 (d, 1H, J_{gem} 12.1 Hz, $\mathrm{OCH_A\underline{H}_BPh}$), 4.61 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.39 (dd, 1H, $J_{5,6e}$ 4.3 Hz, $J_{6e,6a}$ 9.6 Hz, H-6$_e$), 4.30 (dd, 1H, $J_{2,3}$ 4.5 Hz, $J_{3,4}$ 3.0 Hz, H-3), 3.9–3.7 (m, 3H, H-4, H-5, H-6$_a$), 3.35 (m, 1H, $\mathrm{C\underline{H}_AH_BN}$), 2.96 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 4.5 Hz, H-2), 2.65 (m, 1H, $\mathrm{CH_A\underline{H}_BN}$), 1.8–1.7 [m, 4H, $\mathrm{(CH_2)_2}$], 1.36 (s, 3H, $\mathrm{CH_3}$). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ 137.5–126.4 (Ph), 106.6 (OCN), 102.6 ($\mathrm{Ph\underline{C}H}$), 101.4 (C-1), 77.6 (C-4), 71.7 (C-3), 70.9 ($\mathrm{O\underline{C}H_2Ph}$), 69.6 (C-2), 69.3 (C-6), 62.8 (C-5), 55.6 ($\mathrm{CH_2N}$), 38.2, 24.4 [$\mathrm{(CH_2)_2}$], 28.8 ($\mathrm{CH_3}$). HRMS (EI): $[\mathrm{M}]^+$, found 423.205276. $\mathrm{C_{25}H_{29}NO_5}$ requires 423.204573. Anal. calcd for $\mathrm{C_{25}H_{29}NO_5}$: C, 70.90; H, 6.90; N, 3.31. Found: C, 70.63; H, 6.80; N, 3.35.

3.6.3. (2*S*)-2-Phenyl-2,3-propylen-(benzyl 2-amino-4,6-*O*-benzylidene-2,3-dideoxy-β-D-allopyranoside)[2,3-*d*][1,3] oxazolidine 19. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–diethyl ether (8:1) as eluent, yielding 0.15 g (31%) (0.1 g of starting material was recovered); mp 162–163°C; $[\alpha]_D$ −90.9 (*c* 0.5, $\mathrm{CH_2Cl_2}$); MS (CI) *m*/*z* 486 (40%) $[\mathrm{M+H}]^+$. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 7.6–7.2 (m, 15H, 3Ph), 5.53 (s, 1H, $\mathrm{PhC\underline{H}}$), 4.67 (d, 1H, J_{gem} 11.9 Hz, $\mathrm{OC\underline{H}_AH_BPh}$), 4.49 (dd, 1H, $J_{2,3}$ 4.3 Hz, $J_{3,4}$ 3.3 Hz, H-3), 4.32 (d, 1H, J_{gem} 11.9 Hz, $\mathrm{OCH_A\underline{H}_BPh}$), 4.23 (dd, 1H, $J_{5,6e}$ 4.4 Hz, $J_{6e,6a}$ 9.6 Hz, H-6$_e$), 4.08 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 3.77 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{4,5}$ 9.1 Hz, H-4), 3.67 (t, 1H, $J_{5,6a} = J_{6e,6a}$ 9.9 Hz, H-6$_a$), 3.6–3.5 [m, 2H, H-5, $\mathrm{NC\underline{H}_AH_B(CH_2)}$], 3.22 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 4.4 Hz, H-2), 2.88 [m, 1H, $\mathrm{NCH_A\underline{H}_B(CH_2)}$], 2.22 (m, 1H, $\mathrm{NCH_2C\underline{H}_AH_BCH_2}$), 2.03 (m, 1H, $\mathrm{NCH_2CH_A\underline{H}_BCH_2}$), 1.8–1.7 (m, 2H, $\mathrm{NCH_2\,CH_2C\underline{H}_2}$). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ 146.7–125.5 (Ph), 108.6 [$\mathrm{O\underline{C}(Ph)N}$], 102.7 ($\mathrm{Ph\underline{C}H}$), 100.7 (C-1), 77.9 (C-4), 72.9 (C-3), 71.8 ($\mathrm{O\underline{C}H_2Ph}$), 69.7 (C-2), 69.2 (C-6), 62.6 (C-5), 55.8 [$\mathrm{N\underline{C}H_2(CH_2)_2}$], 42.6, 24.9 [$\mathrm{NCH_2(\underline{C}H_2)_2}$]. Anal. calcd for $\mathrm{C_{30}H_{31}NO_5}$: C, 74.21; H, 6.43; N, 2.88. Found: C, 74.07; H, 6.47; N, 2.88.

3.6.4. (2*R*)-2-Methyl-2,3-propylen-(1-dodecyl 2-amino-4,6-*O*-benzylidene-2,3-dideoxy-β-D-allopyranoside)[2,3-*d*] [1,3]oxazolidine 20. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent, yielding 0.40 g (80%); mp 56–57°C; $[\alpha]_D$ −53.3 (*c* 0.5, $\mathrm{CH_2Cl_2}$); MS (CI) *m*/*z* 502 (44%) $[\mathrm{M+H}]^+$. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 7.5–7.3 (m, 5H, Ph), 5.53 (s, 1H, $\mathrm{PhC\underline{H}}$), 4.49 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.37 (dd, 1H, $J_{5,6e}$ 4.5 Hz, $J_{6e,6a}$ 9.6 Hz, H-6$_e$), 4.28 (t, 1H, $J_{2,3} = J_{3,4}$ 4.4 Hz, H-3), 3.9–3.7 (m, 4H, H-4, H-5, H-6$_a$, $\mathrm{OC\underline{H}_AH_BR}$), 3.53 (m, 1H, $\mathrm{OCH_A\underline{H}_BR}$), 3.32 [m, 1H, $\mathrm{(CH_2)_2C\underline{H}_AH_BN}$], 2.86 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 4.4 Hz, H-2), 2.63 [m, 1H, $\mathrm{(CH_2)_2CH_A\underline{H}_BN}$], 1.8–1.6 [m, 4H, $\mathrm{(C\underline{H}_2)CH_2N}$], 1.48 [s, 3H, $\mathrm{OC(CH_3)N}$], 1.24 [m, 20H, $\mathrm{(CH_2)_{10}}$], 0.86 (t, 1H, J 6.5 Hz, $\mathrm{CH_3}$). ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ 137.2–126.4 (Ph), 106.6 [$\mathrm{O\underline{C}(CH_3)N}$], 102.6 ($\mathrm{Ph\underline{C}H}$), 102.4 (C-1), 77.6 (C-4), 71.7 (C-3), 70.3 ($\mathrm{O\underline{C}H_2R}$), 69.7 (C-2), 69.4 (C-6), 62.7 (C-5), 55.8 [$\mathrm{(CH_2)_2\underline{C}H_2N}$]; 38.2, 24.4 [$\mathrm{(\underline{C}H_2)_2CH_2N}$], 31.9–22.7 [$\mathrm{(CH_2)_{10}}$], 29.0 [$\mathrm{OC(\underline{C}H_3)N}$], 14.1 ($\mathrm{CH_3}$). HRMS (CI): $[\mathrm{M+H}]^+$, found 502.353026. $\mathrm{C_{30}H_{48}NO_5}$ requires 502.353249. Anal. calcd for $\mathrm{C_{30}H_{47}NO_5}$: C, 71.82; H, 9.44; N, 2.79. Found: C, 71.59; H, 9.44; N, 2.72.

3.6.5. (2*S*)-2-Phenyl-2,3-propylen-(1-dodecyl 2-amino-4,6-*O*-benzylidene-2,3-dideoxy-β-D-allopyranoside)[2,3-*d*][1,3]oxazolidine 21. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–diethyl ether (10:1) as eluent, yielding 0.35 g (62%); mp 90–91°C; $[\alpha]_D$ +38.5 (*c* 0.5, CH_2Cl_2); MS (CI) *m*/*z* 564 (100%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.7–7.2 (m, 10H, 2Ph), 5.51 (s, 1H, $PhC\underline{H}$), 4.49 (dd, 1H, $J_{2,3}$ 4.3 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.23 (dd, 1H, $J_{5,6e}$ 5.2 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 3.94 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.75 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ 9.4 Hz, H-4), 3.66 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.3 Hz, H-6_a), 3.6–3.5 [m, 3H, H-5, $OC\underline{H}_AH_BR$, $(CH_2)_2C\underline{H}_AH_BN$], 3.24 (m, 1H, $OCH_A\underline{H}_BR$), 3.14 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 4.4 Hz, H-2), 2.89 [m, 1H, $(CH_2)_2CH_A\underline{H}_BN$], 2.3–1.8 [m, 4H, $(C\underline{H}_2)_2CH_2N$], 1.5–1.2 [m, 20H, $(CH_2)_{10}$], 0.87 (t, 1H, *J* 6.9 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 146.9–125.5 (2Ph), 108.5 (OCN), 102.7 ($Ph\underline{C}H$), 100.6 (C-1), 78.1 (C-4), 72.9 (C-3), 70.2 ($O\underline{C}H_2R$), 69.7 (C-2), 69.2 (C-6), 62.6 (C-5), 55.7 $[(CH_2)_2\underline{C}H_2N]$, 42.6, 24.9 $[(\underline{C}H_2)_2CH_2N]$, 31.9–22.6 $[(CH_2)_{10}]$, 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 564.368739. $C_{35}H_{50}NO_5$ requires 564.368899. Anal. calcd for $C_{35}H_{49}NO_5$: C, 74.56; H, 8.76; N, 2.48. Found: C, 74.26; H, 8.56; N, 2.36.

3.7. Formation of γ- and δ-bicyclic lactams from alkyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranosides and γ- or δ-keto-acids

3.7.1. Method A. To a solution of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **5** (0.71 g, 2.0 mmol) in distilled dichloromethane (50 mL), containing 4 Å molecular sieves, 4-acetylbutyric acid (0.52 g, 4.0 mmol) was added, and the reaction mixture was stirred for 2 weeks at room temperature. Then, the solid was removed by filtration through a pad (4 cm diameter×0.5 cm height) of kieselguhr, and the organic phase was washed successively with water, saturated aqueous solution of sodium bicarbonate and water, dried ($MgSO_4$), filtered, and the filtrate evaporated to dryness.

3.7.1.1. γ-Lactam of (*R*)-benzyl 2-amino-4,6-*O*-benzylidene-2-*N*-3-*O*-(3-carboxy-1-methylpropylidene)-2-deoxy-β-D-allopyranoside 22. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (18:10) as eluent, yielding 1.10 g (84%); mp 102–103°C; $[\alpha]_D$ −28.8 (*c* 0.6, CH_2Cl_2); IR (KBr) 1717 cm^{-1}; MS (CI) *m*/*z* 438 (68%) $[M+H]^+$. ^1H NMR (500 MHz, Me_2CO-d_6): δ 7.5–7.2 (m, 10H, 2Ph), 5.7 (s, 1H, $PhC\underline{H}$), 4.87 (d, 1H, J_{gem} 12.5 Hz, $OC\underline{H}_AH_BPh$), 4.69 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.66 (d, 1H, J_{gem} 12.5 Hz; $OCH_A\underline{H}_BPh$), 4.35 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.0 Hz, H-6_e), 4.29 (dd, 1H, $J_{2,3}$ 4.7 Hz, $J_{3,4}$ 3.3 Hz, H-3), 4.12 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 4.7 Hz, H-2), 3.97 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{4,5}$ 9.5 Hz, H-4), 3.86 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.7 Hz, $J_{5,6e}$ 4.8 Hz, H-5), 3.79 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6_a), 2.68 (m, 1H, $CH_2C\underline{H}_AH_BCON$), 2.3–2,1 (m, 3H, $C\underline{H}_2CH_A\underline{H}_BCON$), 1.41 (s, 3H, CH_3). ^{13}C NMR (125 MHz, Me_2CO-d_6): δ 178.7 (C=O), 139.0–127.3 (2Ph), 102.9 ($Ph\underline{C}H$), 101.4 (OCN), 100.4 (C-1), 77.3 (C-4), 76.0 (C-3), 71.0 ($O\underline{C}H_2Ph$), 69.7 (C-6), 64.2 (C-5), 61.1 (C-2), 37.8 ($\underline{C}H_2CH_2CON$), 33.5 ($CH_2\underline{C}H_2CON$), 26.8 (CH_3). Anal. calcd for $C_{25}H_{27}NO_6$: C, 68.63; H, 6.22; N, 3.20. Found: C, 68.44; H, 6.51; N, 3.14.

3.7.1.2. δ-Lactam of (*R*)-benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-2-*N*-3-*O*-(4-carboxy-1-methylbutylidene)-β-D-allopyranoside 24. Only one stereoisomer was obtained, which was purified by column chromatography using dichloromethane–methanol (150:1) as eluent, yielding 0.65 g (72%); mp 88–89°C; $[\alpha]_D$ −57.8 (*c* 0.5, CH_2Cl_2); IR (KBr) 1663 cm^{-1}; MS (CI) *m*/*z* 452 (57%) $[M+H]^+$. ^1H NMR (500 MHz, Me_2CO-d_6): δ 7.5–7.2 (m, 10H, 2Ph), 5.70 (s, 1H, $PhC\underline{H}$), 4.85 (d, 1H, J_{gem} 12.7 Hz, $OC\underline{H}_AH_BPh$), 4.74 (d, 1H, $J_{1,2}$ 6.7 Hz, H-1), 4.63 (d, 1H, J_{gem} 12.7 Hz, $OCH_A\underline{H}_BPh$), 4.57 (dd, 1H, $J_{1,2}$ 6.7 Hz, $J_{2,3}$ 4.8 Hz, H-2), 4.39 (dd, 1H, $J_{2,3}$ 4.8 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.32 (dd, 1H, $J_{5,6e}$ 5.1 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 4.04 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ 9.6 Hz, H-4), 3.92 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 5.1 Hz, H-5), 3.79 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.2 Hz, H-6_a), 2.40 (m, 1H, $CH_2CH_2C\underline{H}_AH_BCON$), 2.28 (m, 1H, $CH_2CH_2CH_A\underline{H}_BCON$), 1.9–1.6 (m, 3H, $C\underline{H}_2C\underline{H}_AH_BCH_2CON$), 1.65 (m, 1H, $CH_2CH_A\underline{H}_BCH_2CON$), 1.34 (s, 3H, CH_3). ^{13}C NMR (125 MHz, Me_2CO-d_6): δ 169.5 (C=O), 139.0–127.3 (2Ph), 103.0 ($Ph\underline{C}H$), 101.2 (C-1), 96.2 (OCN), 77.4 (C-4), 73.3 (C-3), 70.7 ($O\underline{C}H_2Ph$), 69.9 (C-6), 64.3 (C-5), 60.0 (C-2), 34.7 ($CH_2\underline{C}H_2CH_2CON$), 29.1 ($CH_2CH_2\underline{C}H_2CON$), 15.5 ($\underline{C}H_2CH_2CH_2CON$), 26.0 ($CH_3$). Anal. calcd for $C_{26}H_{29}NO_6$: C, 69.16; H, 6.47; N, 3.10. Found: C, 69.13; H, 6.60; N, 2.99.

3.7.1.3. γ-Lactam of (*R*)-1-dodecyl 2-amino-4,6-*O*-benzylidene-2-*N*-3-*O*-(3-carboxy-1-methylpropylidene)-2-deoxy-β-D-allopyranoside 26. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (22:10) as eluent, yielding 1.35 g (87%); mp 72–73°C; $[\alpha]_D$ −36.4 (*c* 0.4, $CHCl_3$); MS (CI) *m*/*z* 516 (72%) $[M+H]^+$. ^1H NMR (200 MHz, Me_2CO-d_6): δ 7.5–7.3 (m, 5H, Ph), 5.64 (s, 1H, $PhC\underline{H}$), 4.64 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.32 (dd, 1H, $J_{5,6e}$ 3.6 Hz, $J_{6e,6a}$ 9.3 Hz, H-6_e), 4.23 (dd, 1H, $J_{2,3}$ 4.7 Hz, $J_{3,4}$ 2.3 Hz, H-3), 4.04 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 4.7 Hz, H-2), 3.9–3.6 (m, 4H, H-4, H-5, H-6_a, $OC\underline{H}_AH_BR$), 3.50 (m, 1H, $OCH_A\underline{H}_BR$), 2.61 (m, 1H, $CH_2C\underline{H}_AH_BCON$), 2.3–2.1 (m, 3H, $C\underline{H}_2CH_A\underline{H}_BCON$), 1.62 (s, 3H, CH_3), 1.30 [m, 20H, $(CH_2)_{10}$], 0,90 (m, 3H, CH_3). ^{13}C NMR (50 MHz, Me_2CO-d_6): δ 178.6 (C=O), 138.7–127.0 (Ph), 102.6 ($Ph\underline{C}H$), 101.4 (C-1), 101.2 (OCN), 77.0 (C-4), 75.7 (C-3), 70.0 (OCH_2R), 69.5 (C-6), 63.8 (C-5), 60.9 (C-2), 37.6 ($\underline{C}H_2CH_2CON$), 33.3 ($CH_2\underline{C}H_2CON$), 32.5–23.9 $[(CH_2)_{10}]$, 27.0 (CH_3), 14.3 $[OCH_2(CH_2)_{10}\underline{C}H_3]$. HRMS (EI): $[M]^{+\bullet}$, found 515.322745. $C_{30}H_{45}NO_6$ requires 515.324689.

3.7.2. Method B. A solution of the alkyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside **5** or **6** (3.0 mmol), the γ- or δ-keto-acid (7.0 mmol) and *p*-toluenesulphonic acid (0.7 mmol) in toluene (150 mL) was stirred under reflux using a Dean–Stark apparatus. When TLC showed that all starting compound had been consumed (~12 h), the reaction mixture was evaporated to dryness. The evaporation residue was dissolved in dichloromethane (200 mL), and the solution was washed successively with water, saturated aqueous sodium bicarbonate solution and water, then dried ($MgSO_4$), filtered, and the filtrate evaporated to dryness. The solid obtained was purified by flash chromatography on silica gel.

3.7.2.1. γ-Lactam of (*S*)-benzyl 2-amino-4,6-*O*-benzylidene-2-*N*-3-*O*-(3-carboxy-1-phenylpropylidene)-2-deoxy-β-D-allopyranoside 23. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (22:10) as eluent, yielding 1.05 g (70%); mp 82–83°C; $[\alpha]_D$ +54.5 (*c* 0.4, CH_2Cl_2); IR (KBr) 1723 cm^{-1}; MS (CI) *m*/*z* 500 (18%) $[M+H]^+$. ^1H NMR (500 MHz, Me_2CO-d_6): δ 7.5–7.3 (m, 15H, 3Ph), 5.68 (s, 1H, $PhC\underline{H}$), 4.70 (d, 1H, J_{gem} 12.3 Hz, $OC\underline{H}_AH_BPh$), 4.51 (t, 1H, $J_{2,3}=J_{3,4}$ 3.4 Hz, H-3), 4.4–4.3 (m, 2H, H-2, $OCH_A\underline{H}_BPh$), 4.22 (dd, 1H, $J_{5,6e}$ 5.3 Hz, $J_{6e,6a}$ 10.3 Hz, H-6_e), 4.18 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.98 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{4,5}$ 9.6 Hz, H-4), 3.72 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.3 Hz, H-6_a), 3.47 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 5.3 Hz, H-5), 2.67 (m, 1H, $CH_2C\underline{H}_AH_BCON$), 2.49 (m, 1H, $C\underline{H}_AH_BCH_2CON$), 2.4–2.3 (m, 2H, $CH_A\underline{H}_BCH_A\underline{H}_BCON$). ^{13}C NMR (125 MHz, Me_2CO-d_6): δ 179.0 (C=O), 139.0–125.1 (3Ph), 103.1 (OCN), 102.8 ($Ph\underline{C}H$), 99.9 (C-1), 77.4 (C-4), 76.8 (C-3), 71.4 ($O\underline{C}H_2Ph$), 69.4 (C-6), 64.1 (C-5), 61.0 (C-2), 39.7 ($\underline{C}H_2CH_2CON$), 32.9 ($CH_2\underline{C}H_2CON$). Anal. calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 71.93; N, 6.17; H, 2.78.

3.7.2.2. δ-Lactam of (*S*)-benzyl 2-amino-4,6-*O*-benzylidene-2-*N*-3-*O*-(4-carboxy-1-phenylbutylidene)-2-deoxy-β-D-allopyranoside 25. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (2:1) as eluent, yielding 1.10 g (71%); mp 154–155°C; $[\alpha]_D$ −41.7 (*c* 0.2, CH_2Cl_2); IR (KBr) 1673 cm^{-1}; MS (CI) *m*/*z* 514 (40%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.2 (m, 10H, 3Ph), 5.53 (s, 1H, $PhC\underline{H}$), 4.92 (dd, 1H, $J_{1,2}$ 6.8 Hz, $J_{2,3}$ 5.0 Hz, H-2), 4.76 (d, 1H, J_{gem} 12.5 Hz, $OC\underline{H}_AH_BPh$), 4.46 (dd, 1H, $J_{2,3}$ 5.0 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.38 (d, 1H, J_{gem} 12.5 Hz, $OCH_A\underline{H}_BPh$), 4.30 (d, 1H, $J_{1,2}$ 6.8 Hz, H-1), 4.19 (dd, 1H, $J_{5,6e}$ 5.3 Hz, $J_{5,6a}$ 10.4 Hz, H-6_e), 3.88 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ 9.6 Hz, H-4), 3.66 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.4 Hz, H-6_a), 3.43 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 5.3 Hz, H-5), 2.5–2.4 (m, 2H, $CH_2CH_2C\underline{H}_2CON$), 2.21 (m, 1H, $CH_2C\underline{H}_AH_BCH_2CON$), 1.86 (m, 1H, $CH_2CH_A\underline{H}_BCH_2CON$), 1.70 (m, 1H, $C\underline{H}_AH_BCH_2CH_2CON$), 1.31 (m, 1H, $CH_A\underline{H}_BCH_2CH_2CON$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.0 (C=O), 142.0–125.4 (3Ph), 102.7 ($PhC\underline{H}$), 99.1 (C-1), 97.9 (OCN), 76.8 (C-4), 73.4 (C-3), 70.6 ($O\underline{C}H_2Ph$), 69.1 (C-6), 62.7 (C-5), 59.3 (C-2), 36.7 ($CH_2\underline{C}H_2CH_2CON$), 29.5 ($CH_2CH_2\underline{C}H_2CON$), 14.5 ($\underline{C}H_2CH_2CH_2CON$). Anal. calcd for $C_{31}H_{31}NO_6$: C, 72.50; H, 6.08; N, 2.73. Found: C, 72.25; H, 6.36; N, 2.55.

3.7.2.3. γ-Lactam of (*S*)-1-dodecyl 2-amino-4,6-*O*-benzylidene-2-*N*-3-*O*-(3-carboxy-1-phenylpropylidene)-2-deoxy-β-D-allopyranoside 27. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (3:1) as eluent, yielding 1.55 g (90%) as a syrup; MS (CI): *m*/*z* 578 (38%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.6–7.3 (m, 10H, 2Ph), 5.53 (s, 1H, $PhC\underline{H}$), 4.39 (m, 1H, H-3), 4.33 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 4.6 Hz, H-2), 4.22 (dd, 1H, $J_{5,6e}$ 5.3 Hz, $J_{6e,6a}$ 10.4 Hz, H-6_e), 4.04 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 3.80 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{4,5}$ 9.5 Hz, H-4), 3.67 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.4 Hz, H-6_a), 3.61 (m, $OC\underline{H}_AH_BR$), 3.52 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 5.3 Hz, H-5), 3.20 (m, $OCH_A\underline{H}_BR$), 2.74 (m, 1H, $CH_2C\underline{H}_AH_BCON$), 2.5–2.4 (m, 3H, $C\underline{H}_2CH_A\underline{H}_BCON$), 0.86 (t, 3H, *J* 6.3 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.6 (C=O), 143.5–124.3 (2Ph), 102.7 ($Ph\underline{C}H$), 102.4 (OCN), 99.1 (C-1), 76.9 (C-4), 76.1 (C-3), 70.2 ($O\underline{C}H_2R$), 69.1 (C-6), 59.9 (C-5), 39.2 ($\underline{C}H_2CH_2CON$), 32.6 ($CH_2\underline{C}H_2CON$), 31.9–22.7 [$(CH_2)_{10}$], 14.1 (CH_3). HRMS (CI): $[M+H]^+$, found 578.347048. $C_{35}H_{48}NO_6$ requires 578.348164.

3.7.2.4. γ-Lactam of (*R*)-benzyl 2-amino-4,6-*O*-benzylidene-2-*N*-3-*O*-(2-carboxybenzylidene)-2-deoxy-β-D-allopyranoside 28. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (28:10) as eluent, yielding 0.80 g (57%); mp 182–183°C; $[\alpha]_D$ −20.0 (*c* 0.6, $CHCl_3$); IR (KBr) 1720 cm^{-1}; MS (CI) *m*/*z* 472 (100%) $[M+H]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.8–7.3 (m, 14H, Ar), 6.14 (s, 1H, OCHN), 5.55 (s, 1H, $PhC\underline{H}$), 4.95 (d, 1H, J_{gem} 12.1 Hz, $OC\underline{H}_AH_BPh$), 4.81 (d, 1H, $J_{1,2}$ 5.8 Hz, H-1), 4.70 (d, 1H, J_{gem} 12.1 Hz, $OCH_A\underline{H}_BPh$), 4.58 (t, 1H, $J_{1,2}=J_{2,3}$ 5.8 Hz, H-2), 4.5–4.4 (m, 2H, H-3, H-6_e), 4.1–4.0 (m, 2H, H-4, H-6_a), 3.78 (m, 1H, H-5). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.6 (C=O), 143.8–123.9 (Ar), 102.5 ($Ph\underline{C}H$), 98.9 (C-1), 92.2 (OCN), 76.8 (C-4), 76.6 (C-3), 70.7 ($O\underline{C}H_2Ph$), 69.5 (C-6), 63.6 (C-5), 59.4 (C-2). Anal. calcd for $C_{28}H_{25}NO_6$: C, 71.32; H, 5.34; N, 2.97. Found: C, 71.05; H, 5.59; N, 2.66.

3.7.2.5. γ-Lactam of (*R*)-benzyl 2-amino-4,6-*O*-benzylidene-2-*N*-3-*O*-[1-(2-carboxyphenyl)ethylidene]-2-deoxy-β-D-allopyranoside 29. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (34:10) as eluent, yielding 1.30 g (90%); mp 107–108°C; $[\alpha]_D$ −73.5 (*c* 0.5, $CHCl_3$); MS (CI) *m*/*z* 486 (65%) $[M+H]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.8–7.3 (m, 14H, Ar), 5.52 (s, 1H, $PhC\underline{H}$), 4.99 (d, 1H, J_{gem} 12.5 Hz, $OC\underline{H}_AH_BPh$), 4.87 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1), 4.74 (d, 1H, J_{gem} 12.5 Hz, $OCH_A\underline{H}_BPh$), 4.5–4.4 (m, 2H, H-3, H-6_e), 4.17 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 3.0 Hz, H-2), 3.97 (m, 1H, H-5), 3.8–3.7 (m, 2H, H-4, H-6_a), 1.56 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 175.2 (C=O), 149.2–123.1 (Ar), 102.5 (C-1), 100.4 (OCN), 98.3 ($Ph\underline{C}H$), 76.7 (C-4), 76.6 (C-3), 70.4 ($O\underline{C}H_2Ph$), 69.2 (C-6), 63.1 (C-5), 62.5 (C-2), 26.7 (CH_3). Anal. calcd for $C_{29}H_{27}NO_6$: C, 71.74; H, 5.61; N, 2.88. Found: C, 71.54;H, 5.85;N, 2.90.

3.8. Reaction of oxazolidines 7, 10, 11, 18 and 22 with lithium aluminium hydride

A solution of either **7**, **10**, **11**, **18** or **22** (0.5 mmol) in dry THF (30 mL) was heated under an argon atmosphere at reflux with stirring. Lithium aluminium hydride solution (1 M) in THF (1.0–5.0 mmol) was added, and the reaction mixture was stirred for 5–48 h (see reaction conditions in Table 1) and was then left to cool to room temperature. Saturated aqueous sodium sulphate solution (0.3–1.5 mL) was added dropwise. The solid was removed by filtration and washed with anhydrous THF and the filtrate was then concentrated to dryness, giving a solid which was purified by column chromatography.

3.8.1. Benzyl 4,6-*O*-benzylidene-2-deoxy-2-ethylmethylamino-β-D-allopyranoside 30. Obtained from compound **7** using the described conditions. Purified by column chromatography using hexane–ethyl acetate–acetone (10:10:1) as eluent, yielding 0.14 g (70%); mp 94–95°C; $[\alpha]_D$ −72.7 (*c* 0.2, CH_2Cl_2); MS (CI) *m*/*z* 400 $[M+H]^+$ (100%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.56 (s, 1H, $\mathrm{PhC\underline{H}}$), 5.06 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.93 (d, 1H, J_{gem} 11.5 Hz, $\mathrm{OC\underline{H}_AH_BPh}$), 4.61 (d, 1H, J_{gem} 11.5 Hz, $\mathrm{OCH_A\underline{H}_BPh}$), 4.38 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.0 Hz, H-6$_e$), 4.32 (t, 1H, $J_{2,3}=J_{3,4}$ 2.6 Hz, H-3), 3.99 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.7 Hz, $J_{5,6e}$ 4.9 Hz, H-5), 3.77 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6$_a$), 3.56 (dd, 1H, $J_{3,4}$ 2.6 Hz, $J_{4,5}$ 9.4 Hz, H-4), 2.8–2.6 (m, 3H, H-2, $\mathrm{NC\underline{H}_2CH_3}$), 2.48 (s, 3H, NCH_3), 1.03 (t, 3H, *J* 7.1 Hz, $\mathrm{NCH_2C\underline{H}_3}$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.2–126.2 (2Ph), 101.7 ($\mathrm{Ph\underline{C}H}$), 99.4 (C-1), 79.5 (C-4), 70.8 ($\mathrm{O\underline{C}H_2Ph}$), 70.1 (C-3), 69.2 (C-6), 64.3 (C-5), 62.8 (C-2), 50.1 ($\mathrm{N\underline{C}H_2CH_3}$), 39.1 ($NCH_3$), 13.2 ($\mathrm{NCH_2\underline{C}H_3}$). HRMS (EI): $[M]^{+\bullet}$, found 399.205079. $C_{23}H_{29}NO_5$ requires 399.204573. Anal. calcd for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.32; N, 3.51. Found: C, 68.93; H, 7.23; N, 3.58.

3.8.2. Benzyl 4,6-*O*-benzylidene-2-deoxy-2-ethylamino-2-*N*-3-*O*-isopropylidene-β-D-allopyranoside 31. Obtained from compound **10** using the described conditions. MS (CI) *m*/*z* 426 (55%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.53 (s, 1H, $\mathrm{PhC\underline{H}}$), 4.89 (d, 1H, J_{gem} 11.6 Hz, $\mathrm{OC\underline{H}_AH_BPh}$), 4.70 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1), 4.63 (d, 1H, J_{gem} 11.5 Hz, $\mathrm{OCH_A\underline{H}_BPh}$), 4,42 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.10 Hz, H-6$_e$), 4.30 (t, 1H, $J_{2,3}=J_{3,4}$ 3.2 Hz, H-3), 4.1–3.6 (m, 3H, H-4, H-5, H-6$_a$), 3.24 (dd, 1H, $J_{1,2}$ 7.3 Hz, $J_{2,3}$ 3.4 Hz, H-2), 2.56 (m, 2H, $\mathrm{NC\underline{H}_2CH_3}$), 1.56, 1.44 [2s, 6H, OC $(CH_3)_2N$], 1.09 (t, 3H, *J* 6.9 Hz, $\mathrm{NCH_2C\underline{H}_3}$).

3.8.3. Benzyl 4,6-*O*-benzylidene-2-deoxy-2-ethylisopropylamino-β-D-allopyranoside 32. Obtained from compound **10** using the described conditions. Purified by column chromatography using hexane–ethyl acetate (1:1) as eluent, yielding 0.12 g (56%) as a syrup; MS (CI) *m*/*z* 428 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.57 (s, 1H, $\mathrm{PhC\underline{H}}$), 4.98 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.93 (d, 1H, J_{gem} 11.3 Hz, $\mathrm{OC\underline{H}_AH_BPh}$), 4.56 (d, 1H, J_{gem} 11.3 Hz, $\mathrm{OCH_A\underline{H}_BPh}$), 4,40 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.0 Hz, H-6$_e$), 4.09 (t, 1H, $J_{2,3}=J_{3,4}$ 2.7 Hz, H-3), 3.99 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.7 Hz, $J_{5,6e}$ 4.9 Hz, H-5), 3.77 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.0 Hz, H-6$_a$), 3.62 (dd, 1H, $J_{3,4}$ 4.9 Hz, $J_{4,5}$ 9.4 Hz, H-4), 3.16 [m, 1H, $\mathrm{NC\underline{H}(CH_3)_2}$], 2.85 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 2.7 Hz, H-2), 2.71 (m, 2H, $\mathrm{NC\underline{H}_2CH_3}$), 1.00 (t, 3H, *J* 7.2 Hz, $\mathrm{NCH_2C\underline{H}_3}$), 0.96 [d, 6H, *J* 6.5 Hz, $\mathrm{NCH(C\underline{H}_3)_2}$]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.3–126.2 (Ph), 101.9 ($\mathrm{Ph\underline{C}H}$), 99.2 (C-1), 79.2 (C-4), 71.3 (C-3), 70.9 ($\mathrm{O\underline{C}H_2Ph}$), 69.3 (C-6), 62.8 (C-5), 61.0 (C-2), 49.5 [$\mathrm{N\underline{C}H(CH_3)_2}$], 40.1 ($\mathrm{N\underline{C}H_2CH_3}$), 21.4, 18.7, [$\mathrm{NCH(\underline{C}H_3)_2}$], 16.6 ($\mathrm{NCH_2\underline{C}H_3}$). HRMS (CI): $[M+H]^+$, found 428.242967. $C_{25}H_{34}NO_5$ requires 428.243699.

3.8.4. Benzyl 4,6-*O*-benzylidene-2-deoxy-2-diethylamino-β-D-allopyranoside 33. Obtained from compound **11** using the described conditions. Purified by column chromatography using hexane–diethyl ether (2:1) as eluent, yielding 0.11 g (53%) as a syrup; MS (CI) *m*/*z* 414 (100%) $[M+H]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.56 (s, 1H, $\mathrm{PhC\underline{H}}$), 5.05 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.92 (d, 1H, J_{gem} 11.5 Hz, $\mathrm{OC\underline{H}_AH_BPh}$), 4.59 (d, 1H, J_{gem} 11.5 Hz, $\mathrm{OCH_A\underline{H}_BPh}$), 4,40 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.1 Hz, H-6$_e$), 4.24 (t, 1H, $J_{2,3}=J_{3,4}$ 2.7 Hz, H-3), 3.98 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.7 Hz, $J_{5,6e}$ 4.8 Hz, H-5), 3.77 (t, 1H, $J_{5,6a}=J_{6e,6a}$ 10.1 Hz, H-6$_a$), 3.59 (dd, 1H, $J_{3,4}$ 2.7 Hz, $J_{4,5}$ 9.3 Hz, H-4), 2.9–2.7 (m, 5H, H-2, $\mathrm{2NC\underline{H}_2CH_3}$), 1.00 (t, 6H, *J* 7.1 Hz, $\mathrm{2NCH_2C\underline{H}_3}$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.3–126.2 (2Ph), 101.8 ($\mathrm{Ph\underline{C}H}$), 99.7 (C-1), 79.6 (C-4), 70.8 ($\mathrm{O\underline{C}H_2Ph}$), 70.6 (C-3), 69.3 (C-6), 62.9 (C-5), 62.7 (C-2), 45.1 ($\mathrm{2N\underline{C}H_2CH_3}$), 13.9 ($\mathrm{2NCH_2\underline{C}H_3}$). HRMS (EI): $[M]^{+\bullet}$, found 413.220264. $C_{24}H_{31}NO_5$ requires 413.220223.

3.8.5. (*S*)-Benzyl 4,6-*O*-benzylidene-2-deoxy-2-(2-methylpyrrolid-1-yl)-β-D-allopyranoside 36. Obtained from compound **18**, using the described conditions. Only one stereoisomer was obtained, which was purified by column chromatography using hexane–ethyl acetate (1:1) as eluent, yielding 0.20 g (94%); mp 66–68°C; $[\alpha]_D$ −60.0 (*c* 0.4, CH_2Cl_2); MS (CI) *m*/*z* 426 $[M+H]^+$ (100%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.57 (s, 1H, $\mathrm{PhC\underline{H}}$), 5.13 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.93 (d, 1H, J_{gem} 11.5 Hz, $\mathrm{OC\underline{H}_AH_BPh}$), 4.59 (d, 1H, J_{gem} 11.5 Hz, $\mathrm{OCH_A\underline{H}_BPh}$), 4.41 (dd, 1H, $J_{5,6e}$ 4.8 Hz, $J_{6e,6a}$ 10.0 Hz, H-6$_e$), 4.22 (t, 1H, $J_{2,3}=J_{3,4}$ 2.6 Hz, H-3), 4.00 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.6 Hz, $J_{5,6e}$ 4.8 Hz, H-5), 3.78 (t, 1H, $J_{5,6e}=J_{6e,6a}$ 10.0 Hz, H-6$_a$), 3.62 (dd, 1H, $J_{3,4}$ 2.6 Hz, $J_{4,5}$ 9.3 Hz, H-4), 3.2–3.1 [m, 2H, $\mathrm{NC\underline{H}(CH_3)}$, $\mathrm{NC\underline{H}_AH_BCH_2CH_2}$], 2.9–2.7 (m, 2H, H-2, $\mathrm{NCH_A\underline{H}_BCH_2CH_2}$), 1.8–1.6 (m, 3H, $\mathrm{NCH_2C\underline{H}_AH_BC\underline{H}_2}$), 1.4–1.3 (m, 1H, $\mathrm{NCH_2CH_A\underline{H}_BCH_2}$), 1.04 (d, 3H, *J* 6.1 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.2–126.2 (2Ph), 101.7 ($\mathrm{Ph\underline{C}H}$), 100.1 (C-1), 79.5 (C-4), 72.5 (C-3), 70.9 ($\mathrm{O\underline{C}H_2Ph}$), 69.3 (C-6), 62.9 (C-5), 60.5 (C-2), 58.6 [$\mathrm{N\underline{C}H(CH_3)}$], 48.5 ($NCH_2$), 31.7, 22.7 [$(CH_2)_2$], 20.2 ($CH_3$). HRMS (CI): $[M+H]^+$, found 426.228071. $C_{25}H_{32}NO_5$ requires 426.228048. Anal. calcd for $C_{25}H_{31}NO_5$: C, 70.56; H, 7.34; N, 3.29. Found: C, 70.28; H, 7.38; N, 3.29.

From compound **22**, using the described conditions two stereoisomers were obtained in 9:1 ratio (80% d.e. for the (*S*)-isomer). The major isomer was isolated by column chromatography using hexane–ethyl acetate (1:1) as eluent, yielding 0.10 g (78%); HRMS (EI): $[M]^{+\bullet}$, found 425.219021. $C_{25}H_{31}NO_5$ requires 425.220223.

3.9. Reaction of oxazolidines 13 and 17 with alkylmagnesium chlorides

A solution of either **13** or **17** (0.5 mmol) in distilled and dried toluene (30 mL) was stirred under an argon atmosphere at reflux. The alkylmagnesium chloride solution in THF (2.0–5.0 mmol) was added, and the reaction mixture was stirred for 4–48 h (see reaction conditions in Table 1). The reaction mixture was diluted with toluene and washed with water, dried ($MgSO_4$), filtered and the filtrate concentrated to dryness. The solid obtained was purified by column chromatography.

3.9.1. Benzyl 4,6-*O*-benzylidene-2-deoxy-2-[ethyl(2,2-dimethyl-1-isopropylprop-1-yl)-amino]-β-D-allopyranoside 34. From compound **13**, using the described conditions, the two stereoisomers were obtained in 7.4:1 ratio (76% d.e.). Column chromatography allowed the purification of the two stereoisomers but not their separation. Yield 0.17 mg (68%); MS (CI) *m*/*z* 498 $[M+H]^+$ (10%). ^1H NMR (200 MHz, $CDCl_3$) (for the major isomer): δ 7.6–7.3 (m, 10H, 2Ph), 5.57 (s, 1H, $PhC\underline{H}$), 5.10 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.98 (d, 1H, J_{gem} 11.3 Hz, $OC\underline{H}_AH_BPh$), 4.60 (d, 1H, J_{gem} 11.3 Hz, $OCH_A\underline{H}_BPh$), 4.43 (dd, 1H, $J_{5,6e}$ 4.9 Hz, $J_{6e,6a}$ 10.2 Hz, H-6_e), 4.25 (t, 1H, $J_{2,3}=J_{3,4}$ 2.6 Hz, H-3), 4.05 (dt, 1H, $J_{4,5}=J_{5,6a}$ 9.9 Hz, $J_{5,6e}$ 4.8 Hz, H-5), 3.79 (t, 1H, $J_{5,6e}=J_{6e,6a}$ 10.0 Hz, H-6_a), 3.62 (dd, 1H, $J_{3,4}$ 2.7 Hz, $J_{4,5}$ 9.7 Hz, H-4), 3.1–2.9 (m, 3H, H-2, $NC\underline{H}_2CH_3$), 2.45 [d, 1H, *J* 3.0 Hz, $(CH_3)_3CC\underline{H}CH(CH_3)_2N$], 2.15 [m, 1H, $(CH_3)_3C$-$CHC\underline{H}(CH_3)_2N$], 1.26 [d, 6H, *J* 7.0 Hz, $(CH_3)_3C$-$CHCH(C\underline{H}_3)_2N$], 1.2–1.0 [m, 12H, $NCH_2C\underline{H}_3$, $(C\underline{H}_3)_3CCHCH(CH_3)_2N$]. Anal. calcd for $C_{30}H_{43}NO_5$: C, 72.40; H, 8.71; N, 2.81. Found: C, 72.28; H, 8.68; N, 2.60.

3.9.2. (*R*)-Benzyl 4,6-*O*-benzylidene-2-deoxy-2-(2-methylpyrrolid-1-yl)-β-D-allopyranoside 35. From compound **17**, using the described conditions, the two stereoisomers were obtained in 6:1 ratio (72% d.e. for (*R*)-isomer). The major isomer was purified by column chromatography using hexane–ethyl acetate (10:15) as eluent, yielding 0.15 g (71%); mp 69–71°C; $[\alpha]_D$ −100.0 (*c* 0.3, CH_2Cl_2); MS (CI) *m*/*z* 426 $[M+H]^+$ (100%). ^1H NMR (200 MHz, $CDCl_3$): δ 7.5–7.3 (m, 10H, 2Ph), 5.56 (s, 1H, $PhC\underline{H}$), 4.96 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.93 (d, 1H, J_{gem} 11.4 Hz, $OC\underline{H}_AH_BPh$), 4.58 (d, 1H, J_{gem} 11.4 Hz, $OCH_A\underline{H}_BPh$), 4.40 (m, 2H, H-3, H-6_e), 4.00 (dt, 1H, $J_{4,5}=J_{5,6a}$ 10.0 Hz, $J_{5,6e}$ 5.1 Hz, H-5), 3.78 (t, 1H, $J_{5,6e}=J_{6e,6a}$ 10.1 Hz, H-6_a), 3.60 (dd, 1H, $J_{3,4}$ 2.5 Hz, $J_{4,5}$ 9.4 Hz, H-4), 3.43 [m, 1H, $NC\underline{H}(CH_3)$], 3.0–2.8 [m, 3H, H-2, $NC\underline{H}_2(CH_2)_2$], 2.0–1.4 [m, 4H, $NCH_2(C\underline{H}_2)$], 0.97 (d, 3H, *J* 6.3 Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.2–126.3 (2Ph), 102.0 ($Ph\underline{C}H$), 99.5 (C-1), 79.4 (C-4), 70.8 ($O\underline{C}H_2Ph$), 69.2 (C-6), 66.6 (C-3), 62.6 (C-2), 62.5 (C-5), 53.6 [$N\underline{C}H(CH_3)$], 49.8 (NCH_2), 32.0, 22.4 [$(CH_2)_2$], 18.2 (CH_3). Anal. calcd for $C_{25}H_{31}NO_5$: C, 70.56; H, 7.34; N, 3.29. Found: C, 70.48; H, 7.26; N, 3.25.

When an identical reaction was carried out at room temperature compound **35** was obtained with d.e. of 76%.

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